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A Perovskite-Like Superstructure of
Co_8S_6 and Ba_6S Clusters

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Abstract

We have prepared single crystals of a new ternary barium cobalt sulfide, $Ba_6Co_{25}S_{27}$ by cooling a melt containing BaS, CoS and Co from 975°C. The structure, determined by single crystal X-ray diffraction, is cubic (Pm3m) with a = 10.033(3)Å, Z=1, and R = 2.6%, R_w = 2.4%. The structure contains an octahedrally coordinated cobalt atom, nearly cubic clusters of eight cobalt atoms, and an unusual arrangement of barium atoms. The electric resistivity and magnetic susceptibility measurements show that $Ba_6Co_{25}S_{27}$ is a poor metal with a resistance minimum at 8K, and Pauli paramagnetic with a small Curie contribution indicating tht either the Co_8 cluster or the octahedrally coordinated cobalt atom has a magnetic moment.

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Introduction

In a previous report[1], we have suggested that the unusual features of the high temperature copper oxide superconductors could be duplicated in solid state compounds with anions other than oxygen, in particular nitrogen and sulfur. In order to test this hypothesis, we are investigating the synthesis, structure and properties of new ternary nitrides and sulfides. Herein, we report our first new ternary sulfide, $Ba_6Co_{25}S_{27}$. We also mention the synthesis of the isostructural compound $Ba_6Ni_{25}S_{27}$.

A first row transition metal to the left of copper may have 3d orbitals with energies similar to the sulfur 3p orbitals necessary for extensive mixing of the states at the Fermi level. Large electropositive cations, such as the heavier alkaline earth metals, may help "enforce" the perovskite related structure of the copper oxide superconductors, as well as increase the oxidizing power of the oxygen[1]. We have chosen to explore the barium cobalt sulfide phase diagram, since these three elements satisfy the above criteria. Since many new barium iron sulfides have been discovered in the past twenty years[2], there promises to be several new barium cobalt sulfides as well.

Only two barium cobalt sulfides have been reported in the literature. Ba_2CoS_3 is isostructural[3] with Ba_2FeS_3, while $BaCoS_2$ has been reported[4] to be isostructural with $BaNiS_2$, the only reported barium nickel sulfide. The former compounds along with all other known barium iron sulfides contain

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FeS_4 tetrahedra sharing edges and/or corners. With the exception of a high pressure polymorph[5] of Ba_2FeS_3, and $BaNiS_2$, in which nickel is pentacoordinate to sulfur in a nearly square pyramidal environment, the transition metal is always tetrahedrally coordinated to sulfur atoms. Furthermore, these compounds do not contain any metal-metal bonding, except for a few barium iron sulfides which contain isolated iron pairs.

The title compound, $Ba_6Co_{25}S_{27}$, is isostructural with the mineral djerfisherite[6] which is similar to Co_9S_8, the mineral pentlandite[7], both of which contain cubic metal clusters and an octahedrally coordinated cobalt atom.

Experimental Section

Sample Preparation. $Ba_6Co_{25}S_{27}$ was first discovered by X-ray powder diffraction of the products produced in high temperature reactions (900°C) of barium sulfide, cobalt sulfide and cobalt powder in graphite containers which were sealed in evacuated quartz tubes. Semi-quantitative electron microprobe analysis of the crystalline product indicated the presence of a new phase with a molar ratio Ba:Co:S of approximately 1:4:5. The new phase, in fact, does not form from reactants heated at this molar ratio; however, it readily forms in mixtures containing less than fifty atom percent sulfur. The crystal used for the structure determination was crystallized from the melt (heated to 975°C, then cooled to 850°C at 2°/hr in a graphite boat and sealed in

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an evacuated quartz tube to prevent reaction with atmospheric oxygen) containing a molar ratio Ba:Co:S of 1:4:4. Single phase polycrystalline $Ba_6Co_{25}S_{27}$ can be made by reacting a pressed pellet (40,000 psi) containing a molar ratio of reactants, BaS:CoS:Co of 6:21:4. The reaction was carried out in an alumina crucible sealed in an evacuated (10 mtorr) quartz tube and heated to 850°C for two days. BaS was purchased from Aesar (99.9%) and CoS was synthesized from the elements (Co: 99.8+%; S: 99.999%). $Ba_6Co_{25}S_{27}$ forms gold metallic crystals which melt congruently at 950°C, contain no ferromagnetic impurity and are largely insensitive to the atmosphere.

$Ba_6Ni_{25}S_{27}$ has been detected by powder X-ray diffraction in multi-phase samples. Reactions containing stoichiometric amounts of BaS, NiS and S show a large impurity of $BaNiS_2$. $Ba_6Ni_{25}S_{27}$ as well as BaS and Ni_3S_2, is seen in reactions slightly deficient in sulfur and with a slight excess of barium. $Ba_6Ni_{25}S_{27}$ has a X-ray powder diffraction pattern similar to $Ba_6Co_{25}S_{27}$, with the same lattice parameters.

X-ray Structural Determination. Diffraction data were collected from an irregularly shaped crystal mounted on a glass fiber, using a Syntex $P2_1$ diffractometer and Mo K-α radiation. Experimental details are listed in Table I. The diffraction peaks were consistent with a primitive cubic unit cell with lattice constant of 10.033Å. The Laue class was found to be m3m and no systematic absences were observed. The possible cubic space groups that give no extinctions are: P23, Pm3, P432, P43m and Pm3m. The structure was

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solved by direct methods and refined using an empirical absorption correction (psi scan) in the highest symmetry space group, Pm3m, with atomic parameters listed in Table II. Refinement in the other groups did not significantly improve the fit. Structure Solution and Refinement were carried out using SHELXTL PLUS Rel. 4.11 software (Siemens). The analytical forms of the scattering factor tables for the neutral atoms[8] were used and all scattering factors were corrected for both real and imaginary components of anomalous dispersion.[9] Selected bond distances and angles for the refined structure are given in Table III.

Table I (Data Collection)

Table II (Atomic Positions)

Table III (Bond Distances and Angles)

Structure Solution. $Ba_6Co_{25}S_{27}$ can be approximately described as cubic close packed layers of barium and sulfur atoms, S(2), S(3) and S(4), with three barium atoms for every thirteen sulfur atoms in each layer. 3/8 of the tetrahedral holes are filled with cobalt atoms, Co(1), as are 1/16 of the octahedral holes between alternating layers, Co(2). The nearest neighbor close packed atoms to both types of cobalt atoms are sulfur atoms only. Between layers in which there are no cobalt atoms in octahedral sites, 1/16 of the octahedral holes contain sulfur atoms, S(1), coordinated only to six barium atoms.

The Co(1) atoms form a nearly cubic cluster with two relatively short Co-Co distances of 2.653(1)Å, and another Co(1)-Co(1) distance of 2.766(2)Å. The

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metal cluster is capped on all faces by sulfur atoms with an average Co-S distance of 2.24Å. Each cube is then bridged to other cubes via eight octahedrally coordinated sulfur atoms connected to the vertices of the cube. As shown in Figure 1, this leads to tetrahedral coordination for the eight cobalt, Co(1), atoms in the cube. The Co(2) atoms are coordinated with perfect octahedral symmetry to six sulfur S(2) atoms (at a distance of 2.369(2)Å), each of which caps a face of a Co(1) cube. Only two opposite faces of the Co(1) cube are capped by S(2) atoms, the other four faces are capped by S(4) atoms which are not coordinated to octahedral cobalt atoms. The Co(1) cube is elongated along the Co(2)-Co(2) axis by .11Å, so that the cube is in fact slightly rectangular.

Six equivalent barium atoms form a perfect octahedron around a central sulfur, with a Ba-S distance of 3.050(1)Å. The Ba-Ba intra-octahedral distances are 4.313(2)Å, while the Ba-Ba inter-octahedral distance is 3.934(2)Å. The sulfur atoms in the close packing layers face and edge cap the barium octahedron with Ba-S distances of 3.217(2)Å and 3.270(2)Å. Each Barium has fourteen near neighbors: four barium atoms and eight sulfur atoms from the close packing, one sulfur in the center of the barium octahedron, and one barium in the next cluster (the short Ba-Ba distance is achieved through a vacant octahedral hole).

The cobalt and barium clusters as individual units form a perovskite-like ($SrTiO_3$) structure. The octahedral cobalt atoms, Co(2), are at the corners

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of the perovskite cell, the cobalt clusters are centered at the midpoint of the cell edges and the barium octahedron is in the center of the cell. A stereoscopic view of the perovskite base and central barium cluster is shown in Figure 2.

Figure 1 (Cobalt Cube)

Figure 2 (Stereoscopic View)

Magnetic Susceptibility Measurement. The Faraday technique was used to measure the magnetic susceptibility of a 58.9 mg powder sample as a function of temperature, in a previously calibrated system[10]. Small amounts of ferromagnetic impurities were removed manually using a strong magnet. The susceptibility was measured as a function of the applied field, and found to be field dependent, indicating a small remaining contamination of ferromagnetic impurity. The ferromagnetic contribution was subtracted from the data by the method of Owen and Honda[11]. The measured magnetic susceptibility for both cooling and heating, shown in Figure 3, is paramagnetic with a small temperature dependence. A peak at 50K due to a small dioxygen impurity from the apparatus' atmosphere was omitted from the data in which it appeared.

Figure 3 (Magnetic Susceptibility vs. Temperature)

Electrical Resistivity Measurement. Four probe resistivity measurements were performed at 13 Hz by lock-in detection. The contacts were shown to be ohmic by the linearity of the I-V characteristic. Resistivities were calculated using the method of van der Pauw[12] for flat samples.

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Cooling and heating curves of the resistivity versus temperature from room temperature to 4.2K, shown in Figure 4, were measured on a polycrystalline pellet (8.0 mm diameter, 1.3 mm thick) sintered at 850°C for 100 hours. Indium electrical contacts were made at four points on the edge of the pellet. Contact resistances were measured to be less than 5 ohms. The room temperature resistivity of the pellet was 3.2×10^{-4} ohm-cm. The resistivity drops sharply at low temperatures, and reaches a resistivity minimum at 8K (see inset).

To confirm the room temperature value, resistivity measurements were also made on a $(0.3 \times 0.2 \times 0.2)$ mm^3 single crystal of $Ba_6Co_{25}S_{27}$. Using four contacts, two with indium metal and two with silver paint, the resistivity of the single crystal was 2.3×10^{-4} ohm-cm at room temperature, indicating that the pellet used for resistivity measurements was well sintered. The resistivity of the single crystal had a similar temperature dependence as the polycrystalline pellet down to 220K, at which point the silver paint contacts failed.

Figure 4 (Electrical Resistivity vs. Temperature)

Results and Discussion

Discussion of Structure. Metal atom clusters such as the one found in $Ba_6Co_{25}S_{27}$ are of interest to molecular chemists, but in a recent review[13] only

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a few nonmolecular solids with discrete octanuclear clusters were mentioned. Co_9S_8 and the mineral pentlandite, $(Fe, Co, Ni)_9S_8$, both contain a perfect cube of metal atoms capped by six sulfur atoms and bridged to four other cubes by eight apical sulfur atoms. The clusters are also bridged by a metal atom octahedrally coordinated to six cube face capping sulfur atoms. Using the notation of Schafer and von Schnering[14], this gives a connectivity pattern $[Co_8S^i_6]S^{a-a}_{8/4}Co^{a-a}_{6/6}$. In this notation, sulfur S^i (inner) atoms bridge metal atoms in the core of a cluster, while sulfur S^a (apical) atoms have only one nearest neighbor metal atom in each cluster, and often bridge between clusters (e.g. S^{a-a}).

$Ba_6Co_{25}S_{27}$ contains similar $[Co_8S^i_6]$ clusters, but one cobalt cluster in four is replaced by a sulfur centered octahedron of barium atoms, $[SBa_6]$. The connectivity is essentially the same except that only one fourth of the octahedral cobalt sites are filled. This gives a connectivity formula of $[SBa_6]S^{i-a}_{8/4}Co^{a-a}_{0/6} + 3([Co_8S^i_6]S^{a-a}_{8/4}Co^{a-a}_{2/6})$. The only other synthetic compound[15] of this type is $K_6LiFe_{24}S_{26}Cl$ where the barium atoms are replaced by potassium, the octahedral cobalt by a lithium, the tetrahedral cobalt atoms by iron, and the octahedral sulfur by chlorine. The mineral djerfisherite,[6] which has been found in meteorites with an approximate chemical formula of $K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$, also has the $Ba_6Co_{25}S_{27}$ structure. Djerfisherite is found with varying amounts of alkali and transition metals. Iron is the primary transition element in djerfisherite, with 8% to 14% by weight copper and less than 1.5% by weight nickel.

The thermal and atmospheric stability of compounds with this structure type and the already known variety of elements that can occupy the different crystallographic sites in this structure leads us to believe that there may be many other compounds of this type with the general formula $A_6M^oM^t_{24}S_{26}X$. A = Ba or K are of appropriate size to replace sulfur atoms in the close packed layers. M^t is a tetrahedrally coordinate metal such as Co, Ni, Fe, or Cu. M^o is an octahedrally coordinate metal which may be the same as M^t. M^o in Co_9S_8 can be replaced by Ru, Rh, Pd[16], and octahedral Ag is found in natural[17] $(Fe,Ni)_8AgS_8$. Although a variety of metals can occupy the M^o site, it is believed that the octahedrally coordinated metals are extremely important to the stability of the metal clusters[18]. X may be S or Cl, which is assumed to substitute in the (1b) site. Preliminary investigations into compounds related to $Ba_6Co_{25}S_{27}$ indicate that the related phase $Ba_6Ni_{25}S_{27}$ also exists. This would be the first case of cube clusters containing only nickel atoms. We have been unable to synthesize the related selenides if they exist.

The tetrahedral cobalt (Co(1)) to sulfur distance in $Ba_6Co_{25}S_{27}$ is slightly larger, averaging 2.24Å (see Table II), than those in Co_9S_8 (2.20Å) and in the thiospinel Co_3S_4 (2.18Å)[7]. The octahedral cobalt (Co(2)) to sulfur distance, 2.369(2)Å, is again slightly longer than the corresponding distances, 2.36Å and 2.34Å, in Co_9S_8 and CoS respectively. These longer distances are expected from the lower average oxidation state of cobalt in $Ba_6Co_{25}S_{27}$ relative to the above binary compounds. Ba - S distances are only somewhat larger

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(3.217(2)Å, 3.270(2)Å) than that in BaS (3.19Å), except for the sulfur at the center of the barium octahedron for which the distance is shortened to 3.050(1)Å. The closest S - S distance is 3.35Å, which is too long to have S - S bonding such as that seen in CoS_2 where the S - S distance is 2.12Å.[19]

Discussion of Physical Properties. To explain the temperature dependent paramagnetism of $Ba_6Co_{25}S_{27}$, the magnetic susceptibility was fit to the Curie-Weiss law, $\chi = \chi_0 + C/(T + \theta)$, at temperatures from 50K to 300K, giving $\chi_0 = 3.0 \times 10^{-6}$ emu/g, $C = 3.2 \times 10^{-4}$ emu-K/g, and $\theta = 42K$. The positive χ_0 is consistent with the observed metallic behavior. The fit is poor at high temperatures with the calculated susceptibility falling off more quickly than that observed as temperature is increased (see inset). This suggests that the Pauli paramagnetic contribution to χ_0 is in fact temperature dependent, and indicates that the value of Weiss constant may not be well determined. Such temperature dependence is expected if there is a high density of states at the Fermi level or significant electron-electron interactions. The unusually high Pauli paramagnetic susceptibility, 3.8×10^{-4} emu/mole of cobalt also indicates that $Ba_6Co_{25}S_{27}$ has a high density of states at the Fermi level and/or significant electron-electron interactions. In comparison, Pd metal has the largest susceptibility of the non magnetic elements, 5.5×10^{-4} emu/mole. The susceptibility of palladium metal is known to be greatly enhanced by electron-electron interactions,[20] so that it is almost ferromagnetic.

The Curie constant, C, gives an effective magnetic moment per cobalt atom of 0.57 Bohr magnetons (μ_B) for $Ba_6Co_{25}S_{27}$. If the paramagnetism were

due to a magnetic iron impurity (at $S = 2$, $g = 2$, $\mu = 4.9\mu_B$, for example), this would require a 1% iron impurity in the cobalt powder which is 99.8% pure. This suggests that the slight Curie paramagnetism is intrinsic to the material. If we assign the entire paramagnetism to the single octahedral cobalt, we calculate a moment of $2.8\mu_B$ per Co(2), consistent with an oxidation state of +1 (Co^I: $S = 1$, $\mu = 2.8\mu_B$; low spin Co^{II}: $S = 1/2$, $\mu = 1.7\mu_B$). Another possibility is to assign the paramagnetism to the metal cluster--doing so yields a moment of $1.63\mu_B$ per Co_8 cluster, which is close to that expected for one unpaired electron per cluster ($S=1/2$, $\mu = 1.7\mu_B$); this could be the case if the octahedral cobalt atoms (Co(2)) are Co^{III} (low spin, $S=0$) which would make each Co_8 cluster a 59 electron unit. Only microscopic measurements, such as electron spin resonance, can determine the origin of this moment unambiguously.

$Ba_6Co_{25}S_{27}$ is a poor metal with a resistivity that is about a hundred times higher than that of copper at room temperature. The resistivity decreases by a factor of 3.5 at low temperatures. Simple metals have resistivity vs. temperature curves that are linear (with a positive slope) or concave upwards at low temperatures. Since $Ba_6Co_{25}S_{27}$ has a resistivity vs. temperature curve that is concave downwards, a scattering mechanism which decreases sharply at low temperatures, is suggested.

This mechanism may involve either magnetic moments in the sample or Umklapp scattering of phonons. If there is a strong correlation between magnetic moments in the bulk sample, then once the magnetic moments

become correlated at low temperatures, electrons are no longer able to undergo spin-flip scattering. Such correlation may by the source of the large θ obtained in the magnetic susceptibility. This phenomenon is seen in metallic compounds that show magnetic order[21] and in correlated systems such as heavy fermion metals.[22] If the resistivity is dominated by Umklapp scattering at high temperatures, we would expect to see an exponential drop in the resistivity at low temperatures.[23] This is probable since the large unit cell makes the Bruillouin zone small so that phonons which undergo Umklapp scattering at the zone boundary are likely to be low in energy. A second order phase transition could also cause this effect, but we would then expect to see an anomaly in the magnetic susceptibility in the same temperature range.

The resistance minimum at 8K may be due to scattering with isolated impurity spins as explained by Kondo[24] for magnetic alloys.

Conclusions

$Ba_6Co_{25}S_{27}$ is the first ternary compound with the Djerfisherite structure. Due to the stability and variability of this structure type, $Ba_6Co_{25}S_{27}$ may be the first of a series of new compounds, many of which would be metallic conductors with unusual electric and magnetic properties as seen in $Ba_6Co_{25}S_{27}$.

Supplementary material available: Structure solution and refinement summary for $Ba_6Co_{25}S_{27}$, including complete tables of bond lengths & angles and anisotropic thermal parameters (7 pages); tables of observed and calculated structure factors are also available (2 pages). Ordering information is given on any current masthead page.

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Figure Captions

Figure 1. Structure and coordination of the cobalt cube cluster. The small black spheres are cobalt atoms, and the larger, shaded spheres are sulfur atoms.

Figure 2. Stereoscopic view of a barium octahedron and its coordination to twelve cobalt clusters. The large, white spheres are barium atoms, the grey spheres are sulfur atoms, and the small black spheres are cobalt atoms.

Figure 3. Magnetic Susceptibility as a function of temperature for $Ba_6Co_{25}S_{27}$. Inset: comparison of the Curie law fit (dashed-dot line) with data.

Figure 4. Electric Resistivity as a function of temperature for $Ba_6Co_{25}S_{27}$. Inset: expansion of data showing resistivity minimum at 8K.

Resistivity (ohm-cm)

Temperature (K)

Resistivity

110x10⁻⁶

Temperature (K)
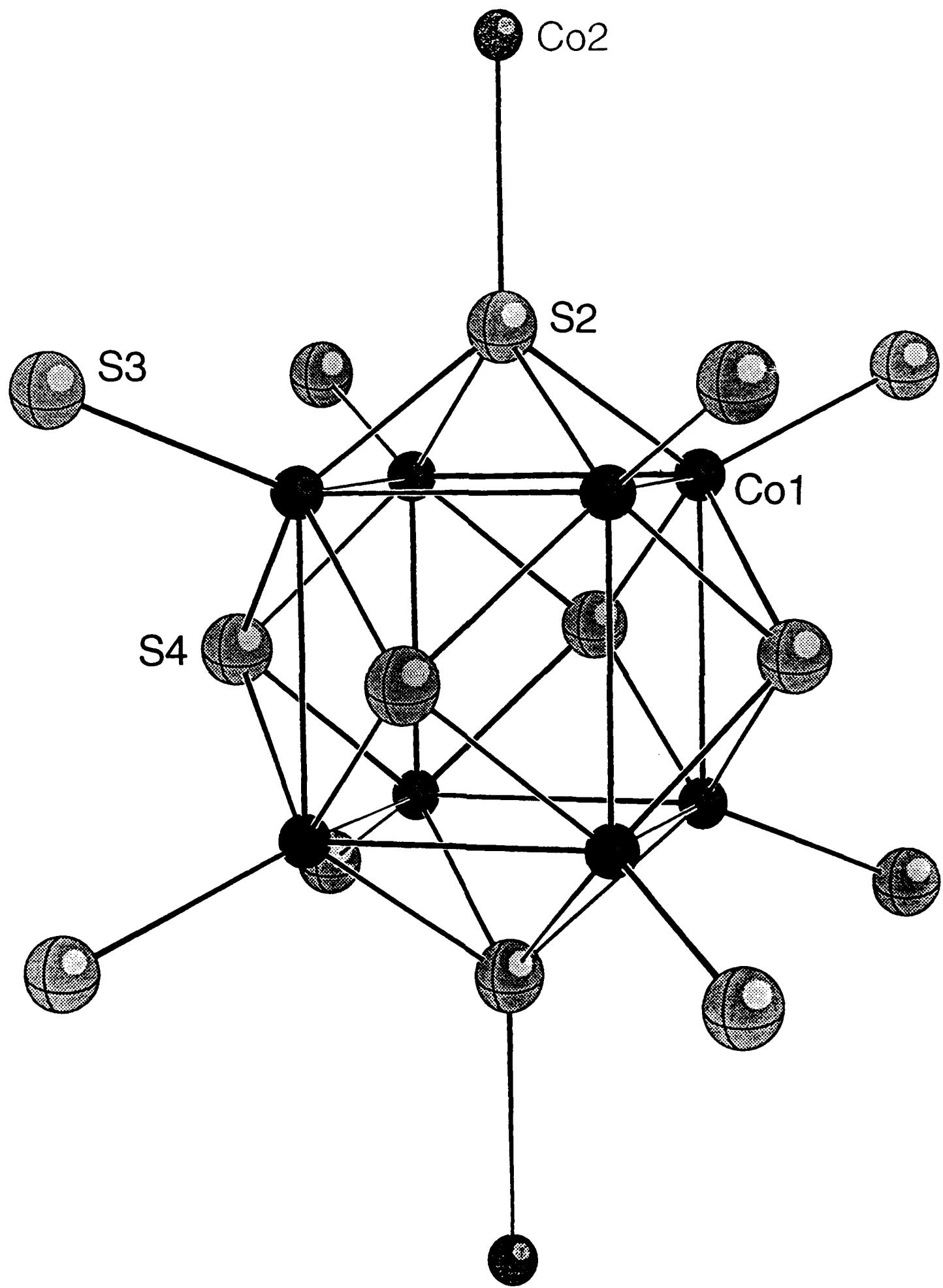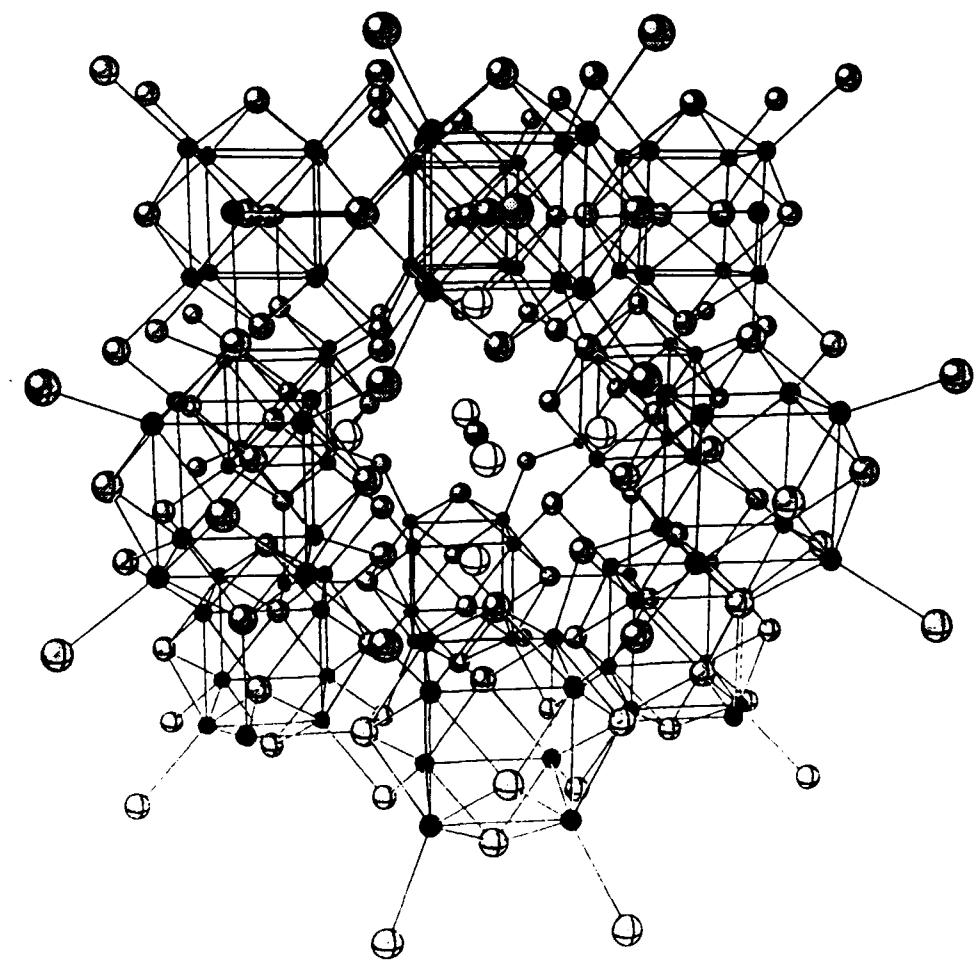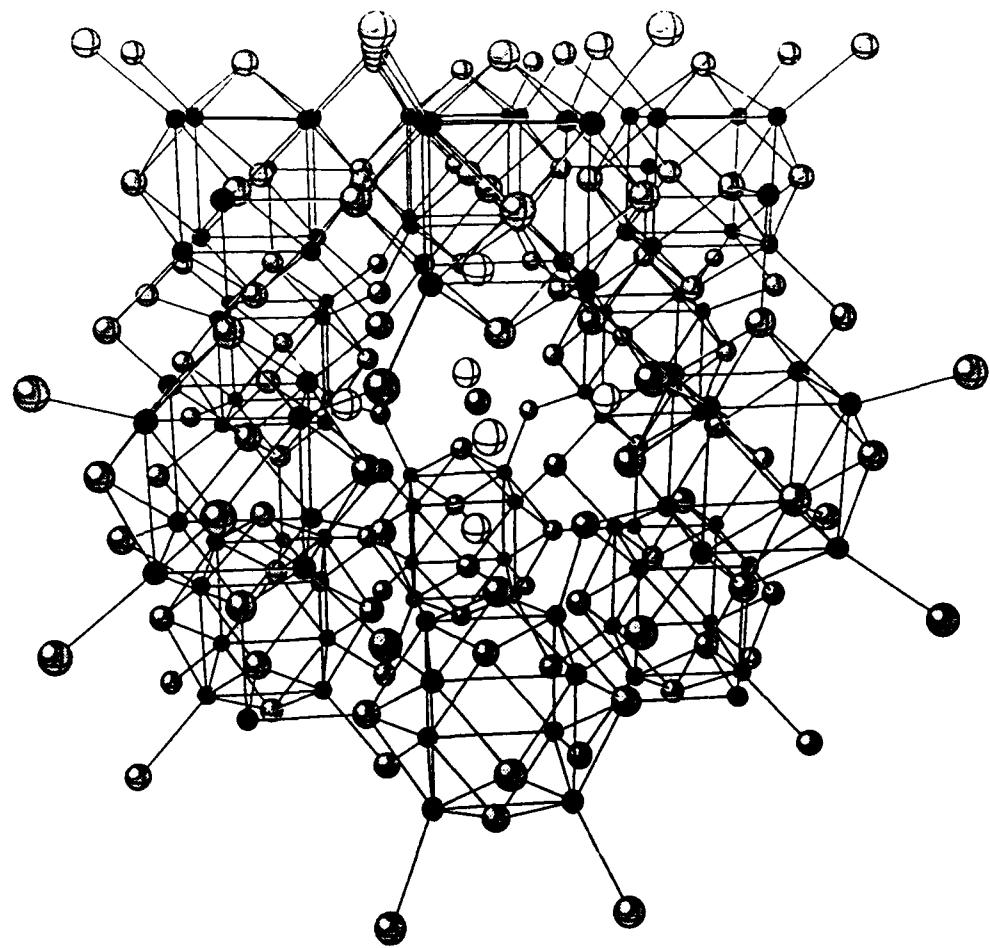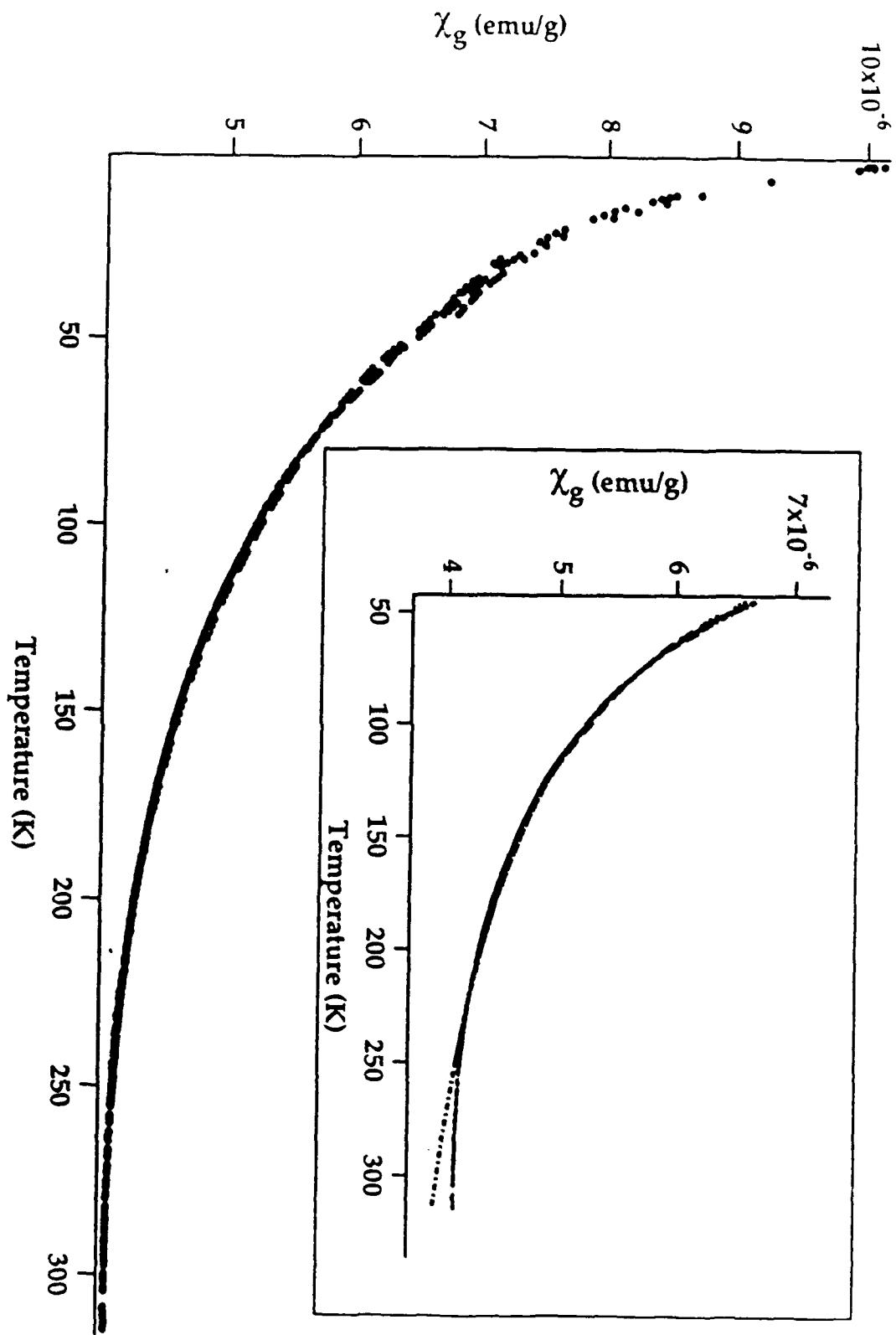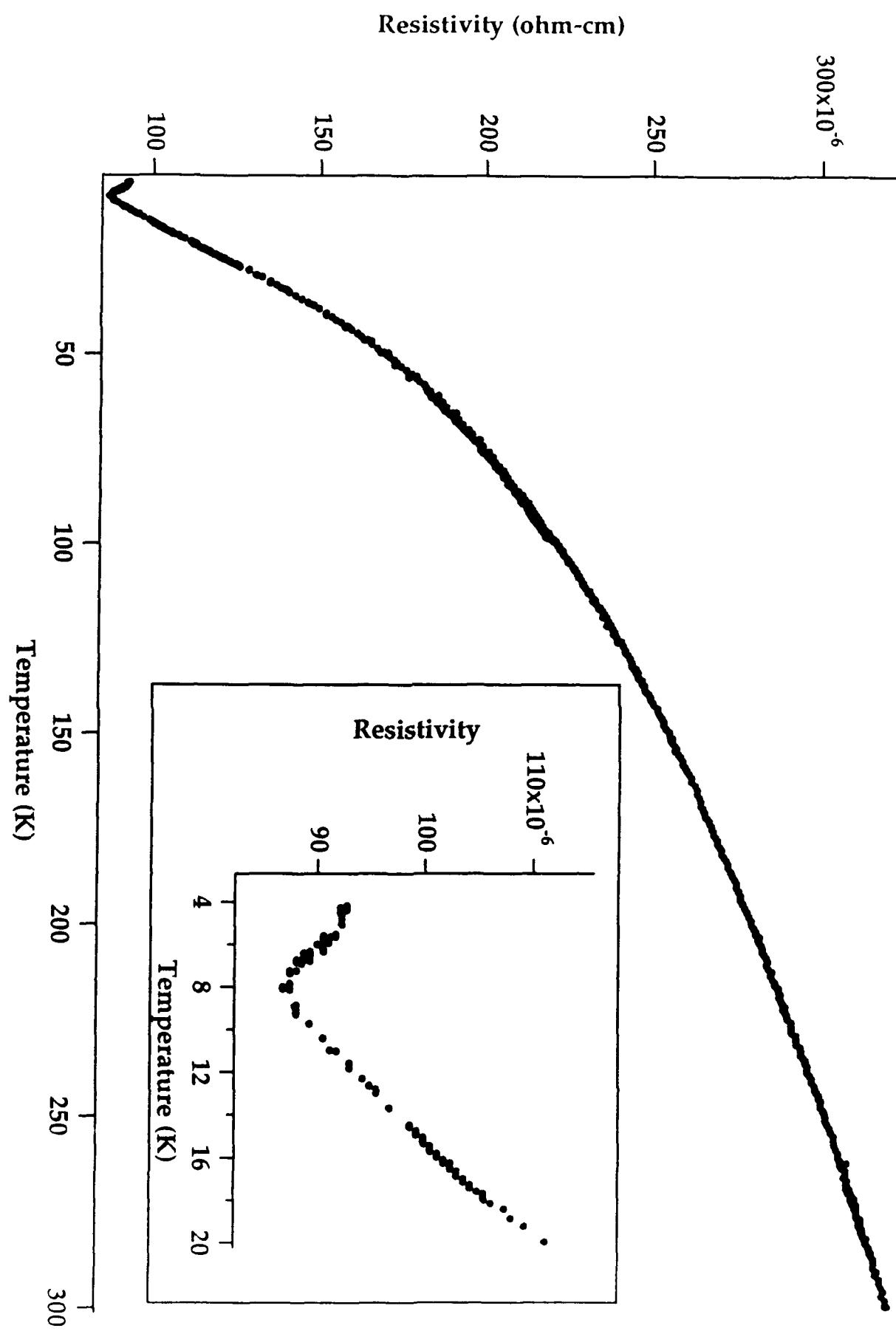
Table I. Single Crystal X-Ray Diffraction Data for $Ba_6Co_{25}S_{27}$

crystal system	cubic
space group	Pm3m (No. 221)
Z	1
a (Å)	10.033(3)
V (Å^3)	1010(1)
density (calculated g/cm^3)	5.201
molecular weight	3162.9
approx. crystal size (mm^3)	0.3 x 0.1 x 0.1
2θ max (deg), scan type	55, ω-2θ
octants measured	(h,k,l);(-h,-k,-l)
x-ray radiation	Mo K-α (λ = 0.71073Å)
monochrometer	graphite
temperature	298K
reflections collected	2768
independent reflections	283 (R_{int} = 3.04%)
observed independent reflections	281 (F > 3.0 σ(F))
absorption coef., μ (mm^{-1})	17.050
R, R_w(%)[1]	2.6, 2.4
F(000)	1443

[1]$R = \Sigma |F_o - F_c| / \Sigma |F_o|$; $R_w = [\Sigma w(|F_o - F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$

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Table II. Positional and Isotropic Thermal Parameters for $Ba_6Co_{25}S_{27}$

atom	site	x	y	z	U_{eq}^* ($Å^2$)
Ba(1)	(6f)	0.5	0.5	0.19603(6)	.0151(2)
Co(1)	(24m)	0.13220(5)	0.36218(7)	0.13220	.0156(2)
Co(2)	(1a)	0.0	0.0	0.0	.0124(4)
S(1)	(1b)	0.5	0.5	0.5	.0146(7)
S(2)	(6e)	0.0	0.2361(2)	0.0	.0136(4)
S(3)	(8g)	0.2767(1)	0.2767	0.2767	.0161(2)
S(4)	(12h)	0.0	0.5	0.2462(2)	.0139(4)

* Equivalent isotropic U defined as one third of the trace of the

orthogonalized Uij tensor

Table III. Selected Atomic Distances (Å) and Angles (deg) for $Ba_6Co_{25}S_{27}$

Co(1)-S(2)	2.262(2)	S(2)-Co(1)-S(3)	123.3(1)
Co(1)-S(3)	2.223(1)	S(2)-Co(1)-S(4)	107.4(0)
Co(1)-S(4)	2 x 2.232(1)	S(3)-Co(1)-S(4)	107.0(1)
		S(4)-Co(1)-S(4)	103.0(1)
Co(2)-S(2)	6 x 2.369(2)		
Co(1)-Co(1)	2 x 2.653(1), 2.766(2)	Co(1)-S(2)-Co(1)	54.1(0), 124.0(1)
Ba(1)-S(1)	3.050(1)		
Ba(1)-S(3)	4 x 3.270(2)		
Ba(1)-S(4)	4 x 3.217(2)		
Ba(1)-Ba(1)	4 x 4.313(2), 3.934(2)		

Supplementary material for

Synthesis, Structure, and Properties of Ba$_6$Co$_{25}$S$_{27}$: A Perovskite-Like Superstructure of Co$_8$S$_6$ and Ba$_6$S Clusters

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Table S1. Structure determination summary for Ba6Co25S27

Crystal Data

Empirical Formula	$Ba_6 Co_{25} S_{27}$
Color; Habit	gold cubes
Crystal Size (mm)	.1 x .1 x .3 (approx.)
Crystal System	Cubic
Space Group	$Pm\bar{3}m$
Unit Cell Dimensions	$a = 10.033(3)$ Å
Volume	1009.8(10) Å^3
Z	1
Formula weight	3162.9
Density(calc.)	5.201 g/cm^3
Absorption Coefficient	17.050 mm^{-1}
F(000)	1443

Data Collection

Diffractometer Used	Syntex P2/1
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	293
Monochromator	Highly oriented graphite crystal
2θ Range	3.0 to 55.0°
Scan Type	2θ-θ
Scan Speed	Variable; 1.50 to 29.30°/min. in ω
Scan Range (ω)	0.50° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 50 reflections
Index Ranges	$0 \leq h \leq 13$, $0 \leq k \leq 13$, $0 \leq \ell \leq 13$; $-13 \leq h \leq 0$, $-13 \leq k \leq 0$, $-13 \leq \ell \leq 13$
Reflections Collected	2768
Independent Reflections	283 (R_{int} = 3.04%)
Observed Ind. Reflections	281 ($F > 3.0\sigma(F)$)
Absorption Correction	Semi-empirical
Min./Max. Transmission	0.0560 / 0.1246

Solution and Refinement

System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	$\chi = 0.00072(10)$, where $F^* = F\ [\ 1 + 0.002\chi F^2/\sin(2\theta)\ ]^{-1/4}$
Weighting Scheme	$w^{-1} = \sigma^2(F)$
Number of Parameters refined	23
Final R indices (obs. data)	R = 2.59 %, wR = 2.42 %
R Indices (all data)	R = 2.63 %, wR = 2.43 %
Goodness-of-Fit	2.43
Largest and Mean Δ/σ	0.004, 0.001
Data-to-Parameter Ratio	12.2:1
Largest Difference Peak	1.66 eÅ^{-3}
Largest Difference Hole	-1.62 eÅ^{-3}

Table S2. Anisotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	17(1)	17(1)	12(1)	0	0	0
Co(1)	14(1)	18(1)	14(1)	-1(1)	0(1)	-1
Co(2)	12(1)	12(1)	12(1)	0	0	0
S(1)	15(1)	15(1)	15(1)	0	0	0
S(2)	14(1)	12(1)	14(1)	0	0	0
S(3)	16(1)	16(1)	16(1)	3(1)	3	3
S(4)	15(1)	15(1)	12(1)	0	0	0

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2 a*^2 U_{11} + \ldots + 2hka*b*U_{12})$$

Table S3. Bond lengths (Å)

Ba(1)-S(1)	3.050	(1)	Ba(1)-S(3)	3.270	(2)
Ba(1)-Ba(1A)	3.934	(2)	Ba(1)-Ba(1C)	4.313	(2)
Ba(1)-Ba(1D)	4.313	(2)	Ba(1)-Ba(1F)	4.313	(2)
Ba(1)-Ba(1G)	4.313	(2)	Ba(1)-S(3A)	3.270	(2)
Ba(1)-S(3B)	3.270	(2)	Ba(1)-S(3C)	3.270	(2)
Ba(1)-S(4A)	3.217	(2)	Ba(1)-S(4B)	3.217	(2)
Ba(1)-S(4C)	3.217	(2)	Ba(1)-S(4D)	3.217	(2)
Co(1)-S(2)	2.262	(2)	Co(1)-S(3)	2.223	(1)
Co(1)-S(4)	2.232	(1)	Co(1)-Co(1B)	2.653	(1)
Co(1)-Co(1D)	2.766	(2)	Co(1)-Co(1E)	2.653	(1)
Co(1)-S(4C)	2.232	(1)	Co(2)-S(2)	2.369	(2)
Co(2)-S(2A)	2.369	(2)	Co(2)-S(2B)	2.369	(2)
Co(2)-S(2C)	2.369	(2)	Co(2)-S(2D)	2.369	(2)
Co(2)-S(2E)	2.369	(2)	S(1)-Ba(1B)	3.050	(1)
S(1)-Ba(1C)	3.050	(1)	S(1)-Ba(1D)	3.050	(1)
S(1)-Ba(1F)	3.050	(1)	S(1)-Ba(1G)	3.050	(1)
S(2)-Co(1B)	2.262	(2)	S(2)-Co(1C)	2.262	(2)
S(2)-Co(1E)	2.262	(2)	S(3)-Ba(1C)	3.270	(2)
S(3)-Ba(1F)	3.270	(2)	S(3)-Co(1F)	2.222	(1)
S(3)-Co(1G)	2.222	(1)	S(4)-Ba(1C)	3.217	(2)
S(4)-Ba(1E)	3.217	(2)	S(4)-Co(1A)	2.232	(1)
S(4)-Co(1D)	2.232	(1)	S(4)-Co(1E)	2.232	(1)

Table S4. Bond angles (°)

S(1)-Ba(1)-S(3)	75.7(1)		S(1)-Ba(1)-Ba(1A)	180.0(1)
S(3)-Ba(1)-Ba(1A)	104.3(1)		S(1)-Ba(1)-Ba(1C)	45.0(1)
S(3)-Ba(1)-Ba(1C)	48.7(1)		Ba(1A)-Ba(1)-Ba(1C)	135.0(1)
S(1)-Ba(1)-Ba(1D)	45.0(1)		S(3)-Ba(1)-Ba(1D)	108.0(1)
Ba(1A)-Ba(1)-Ba(1D)	135.0(1)		Ba(1C)-Ba(1)-Ba(1D)	90.0(1)
S(1)-Ba(1)-Ba(1F)	45.0(1)		S(3)-Ba(1)-Ba(1F)	48.7(1)
Ba(1A)-Ba(1)-Ba(1F)	135.0(1)		Ba(1C)-Ba(1)-Ba(1F)	60.0(1)
Ba(1D)-Ba(1)-Ba(1F)	60.0(1)		S(1)-Ba(1)-Ba(1G)	45.0(1)
S(3)-Ba(1)-Ba(1G)	108.0(1)		Ba(1A)-Ba(1)-Ba(1G)	135.0(1)
Ba(1C)-Ba(1)-Ba(1G)	60.0(1)		Ba(1D)-Ba(1)-Ba(1G)	60.0(1)
Ba(1F)-Ba(1)-Ba(1G)	90.0(1)		S(1)-Ba(1)-S(3A)	75.7(1)
S(3)-Ba(1)-S(3A)	151.3(1)		Ba(1A)-Ba(1)-S(3A)	104.3(1)
Ba(1C)-Ba(1)-S(3A)	108.0(1)		Ba(1D)-Ba(1)-S(3A)	48.7(1)
Ba(1F)-Ba(1)-S(3A)	108.0(1)		Ba(1G)-Ba(1)-S(3A)	48.7(1)
S(1)-Ba(1)-S(3B)	75.7(1)		S(3)-Ba(1)-S(3B)	86.5(1)
Ba(1A)-Ba(1)-S(3B)	104.3(1)		Ba(1C)-Ba(1)-S(3B)	48.7(1)
Ba(1D)-Ba(1)-S(3B)	108.0(1)		Ba(1F)-Ba(1)-S(3B)	108.0(1)
Ba(1G)-Ba(1)-S(3B)	48.7(1)		S(3A)-Ba(1)-S(3B)	86.5(1)
S(1)-Ba(1)-S(3C)	75.7(1)		S(3)-Ba(1)-S(3C)	86.5(1)
Ba(1A)-Ba(1)-S(3C)	104.3(1)		Ba(1C)-Ba(1)-S(3C)	108.0(1)
Ba(1D)-Ba(1)-S(3C)	48.7(1)		Ba(1F)-Ba(1)-S(3C)	48.7(1)
Ba(1G)-Ba(1)-S(3C)	108.0(1)		S(3A)-Ba(1)-S(3C)	86.5(1)
S(3B)-Ba(1)-S(3C)	151.3(1)		S(1)-Ba(1)-S(4A)	127.7(1)
S(3)-Ba(1)-S(4A)	67.0(1)		Ba(1A)-Ba(1)-S(4A)	52.3(1)
Ba(1C)-Ba(1)-S(4A)	115.6(1)		Ba(1D)-Ba(1)-S(4A)	115.6(1)
Ba(1F)-Ba(1)-S(4A)	82.7(1)		Ba(1G)-Ba(1)-S(4A)	172.7(1)
S(3A)-Ba(1)-S(4A)	133.9(1)		S(3B)-Ba(1)-S(4A)	133.9(1)
S(3C)-Ba(1)-S(4A)	67.0(1)		S(1)-Ba(1)-S(4B)	127.7(1)
S(3)-Ba(1)-S(4B)	133.9(1)		Ba(1A)-Ba(1)-S(4B)	52.3(1)
Ba(1C)-Ba(1)-S(4B)	115.6(1)		Ba(1D)-Ba(1)-S(4B)	115.6(1)
Ba(1F)-Ba(1)-S(4B)	172.7(1)		Ba(1G)-Ba(1)-S(4B)	82.7(1)
S(3A)-Ba(1)-S(4B)	67.0(1)		S(3B)-Ba(1)-S(4B)	67.0(1)
S(3C)-Ba(1)-S(4B)	133.9(1)		S(4A)-Ba(1)-S(4B)	104.6(1)
S(1)-Ba(1)-S(4C)	127.7(1)		S(3)-Ba(1)-S(4C)	67.0(1)
Ba(1A)-Ba(1)-S(4C)	52.3(1)		Ba(1C)-Ba(1)-S(4C)	82.7(1)
Ba(1D)-Ba(1)-S(4C)	172.7(1)		Ba(1F)-Ba(1)-S(4C)	115.6(1)
Ba(1G)-Ba(1)-S(4C)	115.6(1)		S(3A)-Ba(1)-S(4C)	133.9(1)
S(3B)-Ba(1)-S(4C)	67.0(1)		S(3C)-Ba(1)-S(4C)	133.9(1)
S(4A)-Ba(1)-S(4C)	68.1(1)		S(4B)-Ba(1)-S(4C)	68.1(1)
S(1)-Ba(1)-S(4D)	127.7(1)		S(3)-Ba(1)-S(4D)	133.9(1)
Ba(1A)-Ba(1)-S(4D)	52.3(1)		Ba(1C)-Ba(1)-S(4D)	172.7(1)
Ba(1D)-Ba(1)-S(4D)	82.7(1)		Ba(1F)-Ba(1)-S(4D)	115.6(1)
Ba(1G)-Ba(1)-S(4D)	115.6(1)		S(3A)-Ba(1)-S(4D)	67.0(1)
S(3B)-Ba(1)-S(4D)	133.9(1)		S(3C)-Ba(1)-S(4D)	67.0(1)
S(4A)-Ba(1)-S(4D)	68.1(1)		S(4B)-Ba(1)-S(4D)	68.1(1)
S(4C)-Ba(1)-S(4D)	104.6(1)		S(2)-Co(1)-S(3)	123.3(1)
S(2)-Co(1)-S(4)	107.4(1)		S(3)-Co(1)-S(4)	107.0(1)
S(2)-Co(1)-Co(1B)	54.1(1)		S(3)-Co(1)-Co(1B)	130.7(1)
S(4)-Co(1)-Co(1B)	120.8(1)		S(2)-Co(1)-Co(1D)	124.0(1)
S(3)-Co(1)-Co(1D)	112.7(1)		S(4)-Co(1)-Co(1D)	51.7(1)
Co(1B)-Co(1)-Co(1D)	90.0(1)		S(2)-Co(1)-Co(1E)	54.1(1)
S(3)-Co(1)-Co(1E)	130.7(1)		S(4)-Co(1)-Co(1E)	53.5(1)
Co(1B)-Co(1)-Co(1E)	90.0(1)		Co(1D)-Co(1)-Co(1E)	90.0(1)
S(2)-Co(1)-S(4C)	107.4(1)		S(3)-Co(1)-S(4C)	107.0(1)
S(4)-Co(1)-S(4C)	103.0(1)		Co(1B)-Co(1)-S(4C)	53.5(1)
Co(1D)-Co(1)-S(4C)	51.7(1)		Co(1E)-Co(1)-S(4C)	120.8(1)

S(2)-Co(2)-S(2A)	180.0(1)	S(2)-Co(2)-S(2B)	90.0(1)
S(2A)-Co(2)-S(2B)	90.0(1)	S(2)-Co(2)-S(2C)	90.0(1)
S(2A)-Co(2)-S(2C)	90.0(1)	S(2B)-Co(2)-S(2C)	180.0(1)
S(2)-Co(2)-S(2D)	90.0(1)	S(2A)-Co(2)-S(2D)	90.0(1)
S(2B)-Co(2)-S(2D)	90.0(1)	S(2C)-Co(2)-S(2D)	90.0(1)
S(2)-Co(2)-S(2E)	90.0(1)	S(2A)-Co(2)-S(2E)	90.0(1)
S(2B)-Co(2)-S(2E)	90.0(1)	S(2C)-Co(2)-S(2E)	90.0(1)
S(2D)-Co(2)-S(2E)	180.0(1)	Ba(1)-S(1)-Ba(1B)	180.0(1)
Ba(1)-S(1)-Ba(1C)	90.0(1)	Ba(1B)-S(1)-Ba(1C)	90.0(1)
Ba(1)-S(1)-Ba(1D)	90.0(1)	Ba(1B)-S(1)-Ba(1D)	90.0(1)
Ba(1C)-S(1)-Ba(1D)	180.0(1)	Ba(1)-S(1)-Ba(1F)	90.0(1)
Ba(1B)-S(1)-Ba(1F)	90.0(1)	Ba(1C)-S(1)-Ba(1F)	90.0(1)
Ba(1D)-S(1)-Ba(1F)	90.0(1)	Ba(1)-S(1)-Ba(1G)	90.0(1)
Ba(1B)-S(1)-Ba(1G)	90.0(1)	Ba(1C)-S(1)-Ba(1G)	90.0(1)
Ba(1D)-S(1)-Ba(1G)	90.0(1)	Ba(1F)-S(1)-Ba(1G)	180.0(1)
Co(1)-S(2)-Co(2)	124.0(1)	Co(1)-S(2)-Co(1B)	71.8(1)
Co(2)-S(2)-Co(1B)	124.0(1)	Co(1)-S(2)-Co(1C)	112.0(1)
Co(2)-S(2)-Co(1C)	124.0(1)	Co(1B)-S(2)-Co(1C)	71.8(1)
Co(1)-S(2)-Co(1E)	71.8(1)	Co(2)-S(2)-Co(1E)	124.0(1)
Co(1B)-S(2)-Co(1E)	112.0(1)	Co(1C)-S(2)-Co(1E)	71.8(1)
Ba(1)-S(3)-Co(1)	91.2(1)	Ba(1)-S(3)-Ba(1C)	82.5(1)
Co(1)-S(3)-Ba(1C)	91.2(1)	Ba(1)-S(3)-Ba(1F)	82.5(1)
Co(1)-S(3)-Ba(1F)	171.6(1)	Ba(1C)-S(3)-Ba(1F)	82.5(1)
Ba(1)-S(3)-Co(1F)	171.6(1)	Co(1)-S(3)-Co(1F)	94.5(1)
Ba(1C)-S(3)-Co(1F)	91.2(1)	Ba(1F)-S(3)-Co(1F)	91.2(1)
Ba(1)-S(3)-Co(1G)	91.2(1)	Co(1)-S(3)-Co(1G)	94.5(1)
Ba(1C)-S(3)-Co(1G)	171.6(1)	Ba(1F)-S(3)-Co(1G)	91.2(1)
Co(1F)-S(3)-Co(1G)	94.5(1)	Co(1)-S(4)-Ba(1C)	92.4(1)
Co(1)-S(4)-Ba(1E)	140.3(1)	Ba(1C)-S(4)-Ba(1E)	75.4(1)
Co(1)-S(4)-Co(1A)	118.3(1)	Ba(1C)-S(4)-Co(1A)	140.3(1)
Ba(1E)-S(4)-Co(1A)	92.4(1)	Co(1)-S(4)-Co(1D)	76.6(1)
Ba(1C)-S(4)-Co(1D)	92.4(1)	Ba(1E)-S(4)-Co(1D)	140.3(1)
Co(1A)-S(4)-Co(1D)	72.9(1)	Co(1)-S(4)-Co(1E)	72.9(1)
Ba(1C)-S(4)-Co(1E)	140.3(1)	Ba(1E)-S(4)-Co(1E)	92.4(1)
Co(1A)-S(4)-Co(1E)	76.6(1)	Co(1D)-S(4)-Co(1E)	118.3(1)

Observed and calculated structure factors for BaCo$_{25}$S$_{27}$

h	k	l	Fo	Fc	s	h	k	l	Fo	Fc	s	h	k	l	Fo	Fc	s	h	k	l	Fo	Fc	s	h	k	l	Fo	Fc	s
0	0	1	31	26	1	0	1	6	19	-18	1	1	7	7	178	-180	1	1	3	9	27	26	1	4	5	10	24	-23	1
0	1	1	32	-32	1	1	1	6	28	27	1	2	7	7	10	9	2	2	3	9	51	52	0	5	5	10	6	1	-2
1	1	1	66	-63	1	0	2	6	41	39	0	3	7	7	69	67	1	3	3	9	112	-113	1	0	6	10	44	43	1
0	0	2	71	72	2	1	2	6	14	12	1	4	7	7	148	145	2	0	4	9	93	-94	1	1	6	10	62	-61	1
0	1	2	23	22	0	2	2	6	210	-210	2	5	7	7	38	36	1	1	4	9	15	12	1	2	6	10	35	-34	1
1	1	2	75	-72	1	0	3	6	193	-198	2	6	7	7	61	58	1	2	4	9	79	81	1	3	6	10	79	-78	1
0	2	2	15	6	1	1	3	6	106	106	1	7	7	7	186	-173	5	3	4	9	30	29	1	4	6	10	74	72	1
1	2	2	124	126	2	2	3	6	39	-39	0	0	0	8	464	469	6	4	4	9	43	41	1	5	6	10	10	-9	2
2	2	2	463	-456	12	3	3	6	142	141	1	0	1	8	97	99	1	0	5	9	43	42	0	0	7	10	119	-118	1
0	0	3	295	-298	8	0	4	6	34	34	1	1	1	8	124	-127	1	1	5	9	84	83	1	1	7	10	71	70	1
0	1	3	242	233	3	1	4	6	39	-39	0	0	2	8	23	-23	1	2	5	9	65	-66	1	2	7	10	49	-47	1
1	1	3	190	183	1	2	4	6	14	9	1	1	2	8	105	106	1	3	5	9	15	10	2	3	7	10	91	87	1
0	2	3	112	-111	1	3	4	6	60	-59	0	2	2	8	137	-137	1	4	5	9	10	2	2	4	7	10	32	-30	1
1	2	3	35	34	0	4	4	6	178	176	1	0	3	8	69	-70	1'	5	5	9	54	52	1	0	8	10	7	-3	2
2	2	3	52	51	1	0	5	6	18	-17	1	1	3	8	35	34	1	0	6	9	8	1	2	1	8	10	9	-6	2
0	3	3	124	125	2	1	5	6	15	-10	1	2	3	8	46	46	0	1	6	9	33	33	1	2	8	10	24	-21	1
1	3	3	314	-318	5	2	5	6	47	47	0	3	3	8	35	-34	1	2	6	9	12	-8	2	0	0	11	73	-73	1
2	3	3	98	97	1	3	5	6	60	60	0	0	4	8	81	-80	1	3	6	9	80	78	1	0	1	11	31	31	1
3	3	3	56	55	2	4	5	6	72	70	0	1	4	8	34	34	1	4	6	9	9	-5	2	1	1	11	128	131	1
0	0	4	15	0	1	5	5	6	44	-44	1	2	4	8	10	-7	1	5	6	9	10	-5	2	0	2	11	18	-17	1
0	1	4	139	-136	2	0	6	6	130	130	1	3	4	8	61	60	0	6	6	9	33	-32	1	1	2	11	42	-43	1
1	1	4	47	46	0	1	6	6	34	-34	1	4	4	8	290	288	3	0	7	9	27	27	1	2	2	11	76	79	1
0	2	4	116	116	1	2	6	6	103	-102	1	0	5	8	25	25	1	1	7	9	34	-30	1	0	3	11	8	6	1
1	2	4	110	108	1	3	6	6	115	-113	1	1	5	8	72	-73	1	2	7	9	46	46	1	1	3	11	94	-94	1
2	2	4	87	-85	1	4	6	6	21	20	1	2	5	8	144	145	1	3	7	9	31	-29	1	2	3	11	22	-21	1
0	3	4	15	11	1	5	6	6	23	-21	1	3	5	8	76	-74	1	4	7	9	14	12	1	3	3	11	78	79	1
1	3	4	28	-27	1	6	6	6	19	-18	3	4	5	8	138	136	1	5	7	9	60	57	1	0	4	11	69	70	1
2	3	4	62	-61	1	0	0	7	5	9	-2	5	5	8	117	-114	1	6	7	9	72	68	1	1	4	11	68	-68	1
3	3	4	243	242	3	0	1	7	9	5	1	0	6	8	124	126	1	0	8	9	56	56	1	2	4	11	9	-3	2
0	4	4	710	705	9	1	1	7	131	-133	1	1	6	8	59	60	1	1	8	9	40	-40	1	3	4	11	64	65	1
1	4	4	110	113	1	0	2	7	125	-126	1	2	6	8	73	-72	1	2	8	9	74	72	1	4	4	11	19	-16	2
2	4	4	31	-31	1	1	2	7	17	15	1	3	6	8	39	-37	1	3	8	9	7	2	2	0	5	11	61	-61	1
3	4	4	115	-114	1	2	2	7	62	61	1	4	6	8	31	-30	1	4	8	9	18	16	1	1	5	11	21	20	1
4	4	4	94	-93	1	0	3	7	246	250	3	5	6	8	55	53	1	5	8	9	47	-43	1	2	5	11	42	-40	1
0	0	5	169	-173	4	1	3	7	82	82	1	6	6	8	21	6	4	0	9	9	68	69	1	3	5	11	72	72	0
0	1	5	36	36	1	2	3	7	41	41	0	0	7	8	33	33	1	1	9	9	8	10	3	4	5	11	42	-41	1
1	1	5	229	227	3	3	3	7	294	-295	2	1	7	8	72	-73	1	2	9	9	29	-27	1	0	6	11	74	-73	1
0	2	5	143	142	1	0	4	7	125	-126	1	2	7	8	20	18	1	0	0	10	66	68	0	1	6	11	7	3	2
1	2	5	108	-107	1	1	4	7	86	87	0	3	7	8	80	76	1	0	1	10	97	-99	0	2	6	11	24	24	1
2	2	5	119	119	1	2	4	7	36	-36	1	4	7	8	21	-19	1	1	1	10	53	53	1	3	6	11	23	21	1
0	3	5	8	3	1	3	4	7	27	26	1	5	7	8	24	-22	1	0	2	10	49	49	1	0	7	11	91	90	1
1	3	5	54	-54	0	4	4	7	52	52	1	6	7	8	8	0	2	1	2	10	7	-3	1	0	0	12	16	-12	1
2	3	5	9	3	1	0	5	7	37	37	0	7	7	8	41	-39	1	2	2	10	92	-94	1	0	1	12	6	-1	1
3	3	5	70	65	1	1	5	7	120	121	1	0	8	8	207	209	2	0	3	10	73	-74	1	1	1	12	15	-14	2
0	4	5	82	82	1	2	5	7	8	7	1	1	8	8	124	124	1	1	3	10	78	80	1	0	2	12	44	44	0
1	4	5	81	-82	1	3	5	7	131	-130	1	2	8	8	79	-78	2	2	3	10	68	-69	1	1	2	12	58	59	1
2	4	5	135	137	1	4	5	7	54	-54	1	3	8	8	29	28	1	3	3	10	138	141	1	2	2	12	97	-99	1
3	4	5	35	34	0	5	5	7	37	37	1	4	8	8	101	-96	1	0	4	10	233	236	2	0	3	12	13	-13	1
4	4	5	17	-16	1	0	6	7	93	-95	1	5	8	8	92	86	1	1	4	10	7	1	1	1	3	12	40	-41	1
0	5	5	20	-23	1	1	6	7	63	63	1	6	8	8	28	24	2	2	4	10	10	-8	1	2	3	12	18	17	1
1	5	5	96	96	1	2	6	7	31	-30	1	0	1	9	46	47	0	3	4	10	103	-104	1	3	3	12	64	65	1
2	5	5	146	-147	1	3	6	7	108	106	1	1	1	9	18	14	1	4	4	10	11	6	2	0	4	12	193	195	2
3	5	5	151	150	1	4	6	7	111	-108	1	0	2	9	48	49	1	0	5	10	6	-2	2	1	4	12	58	58	1
4	5	5	45	-44	1	5	6	7	46	44	1	1	2	9	26	-27	1	1	5	10	22	20	1	2	4	12	13	-10	1
5	5	5	179	175	5	6	6	7	65	-62	1	2	2	9	33	32	1	2	5	10	20	21	1	3	4	12	23	-21	1
0	0	6	328	337	7	0	7	7	65	66	1	0	3	9	72	73	0	3	5	10	56	56	0	0	5	12	70	69	1

Observed and calculated structure factors for $BaCo_{25}S_{27}$

h	k	l	Fo	Fc	s		h	k	l	Fo	Fc	s		h	k	l	Fo	Fc	s		h	k	l	Fo	Fc	s		h	k	l	Fc	s
1	5	12	72	-72	1		0	0	13	111	-112	1		0	1	13	57	57	0													

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